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16. ABSTRACT

Severe corrosion of reinforcing steel and concrete deterioration in reinforced concrete bridge decks caused by salt applied to the decks to control ice and snow has prompted a search for noncorrosive deicing chemical suitable for maintenance use. Seventeen candidate chemicals have been evaluated. Tetrapotassium pyrophosphate (TKPP) exhibited good frost preventing properties and two years of limited field testing on bridge decks is reported. A skidding car method of coefficient of friction is presented. The test results of sodium formate used as a deicer and its detrimental effect on concrete is evaluated.

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HIGHWAY RESEARCH REPORT

FURTHER EVALUATION OF DEICING CHEMICALS

74-01

STATE OF CALIFORNIA

BUSINESS AND TRANSPORTATION AGENCY

DEPARTMENT OF TRANSPORTATION

DIVISION OF HIGHWAYS

TRANSPORTATION LABORATORY

RESEARCH REPORT

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STATE OF CALIFORNIA—BUSINESS AND TRANSPORTATION AGENCY RONALD REAGAN, Governor

DEPARTMENT OF TRANSPORTATION
DIVISION OF HIGHWAYS
TRANSPORTATION LABORATORY
5900 FOLSOM BLVD., SACRAMENTO 95819

January, 1974

Trans. Lab No. 635197- 2
FHWA No. B-4-3

Mr. R. J. Datel
State Highway Engineer

Dear Sir:

Submitted herewith is a final research report titled:

FURTHER EVALUATION OF DEICING CHEMICALS

Project Supervisor and Co-Investigator
J. A. Halterman

Principal Investigator
R. F. Stratfull

Under the Supervision of
D. L. Spellman

Very truly yours,

JOHN L. BEATON
Chief, Transportation Laboratory

Attachment

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This project was performed in cooperation with the U. S. Department of Transportation, Federal Highway Administration, Agreement No. B-4-3.

The contents of this report reflect the views of the Transportation Laboratory which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the State of California or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

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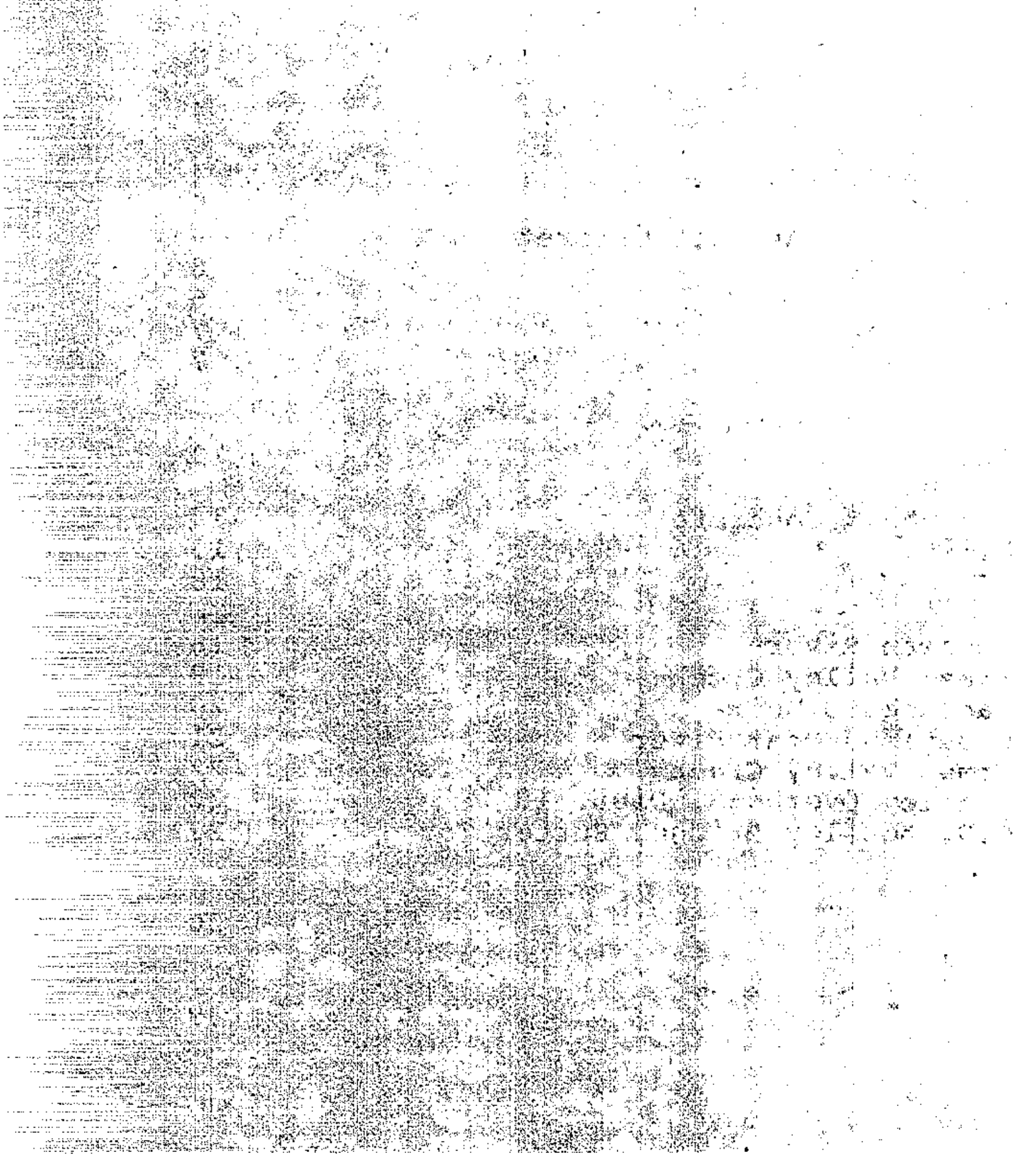

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INTRODUCTION

Considerable attention[1,3,4,5,11] has been given to the problem of bridge deck deterioration. In general, the results have shown that one of the most significant causes of rusting of the steel and spalling concrete is the use of salt for snow, ice, and frost control on bridge decks. In this respect, studies have been made to determine the feasibility of (1) the heating of bridge decks and thus reduce or eliminate the need for salt to prevent frosting or icing; (2) use of waterproof membranes wherein salt is prevented from coming in contact with the concrete; (3) use of polymers or other penetration type sealers which may make concrete itself sufficiently waterproof that chlorides may not be able to penetrate the concrete in a short time; and (4) studies of use of chemicals other than chloride which not only will control ice and frost, but will be noncorrosive to either the concrete imbedded steel or the concrete itself[2,6,7,8,9].

In a previous study, a total of 17 different potential deicing chemicals were subjected to various laboratory and field tests[11]. Of these 17 chemicals, only sodium formate and tetrapotassium pyrophosphate were found to be reasonably effective alternative deicing chemicals and yet not be any more toxic or ecologically harmful than sodium chloride. However, sodium formate was found to attack concrete by the apparent mechanism of its crystal formation being of greater volume than the concrete capillaries and thus resulting in damage when alternately wet and dried. The same is true of sodium chloride, but at a lesser rate of distress.

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As a result of the initial study[11], tetrapotassium pyrophosphate (TKPP) was tested by highway maintenance forces at selected bridge locations. These bridges were "salted" to prevent frosting and not for the purpose of snow and ice removal. The previous work had shown that a liquid solution of TKPP could melt about one inch (2.5 cm) of continuously falling snow on a pavement. However, because it costs about 15 times more than salt, its use was considered as most appropriate for those locations where only the bridge deck is "salted". Initially the work was primarily oriented toward a laboratory search for alternative deicing chemicals with research personnel performing a minimum field evaluation to confirm the test results. This report presents the results of the use of the chemicals by maintenance personnel to determine if there were any operational difficulties. Also, the previous work indicated that the frost prevention abilities of TKPP was severely limited when the temperature was less than about 25°F (-4°C). Although TKPP was found to be mildly corrosive to steel, its corrosiveness could be reduced by the addition of about 2% by weight of calcium hydroxide to the solution. This addition of lime is not considered necessary for use on a bridge deck, but only useful when corrosion of vehicles or containers is considered. Apparently TKPP does not penetrate structural quality concrete and cause corrosion of the imbedded steel. This is evidenced by the fact that the removal of the effects of the TKPP seems to be only related to "tracking" of the material to the abuting pavement and the washing effect of rainfall. Also, during dry weather, crystals of the chemical are observed on the surface of the pavement.

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This report is the finalization of the original work wherein the results of two years of field testing at selected locations are related, as well as further evaluations of skid resistance and corrosion.

IMPLEMENTATION

The utilization of the alternative deicing chemicals has been recommended to the Office of Structures and the Maintenance Branch of the California Department of Transportation.

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SUMMARY AND CONCLUSIONS

Field Tests - Frost Prevention

Based on a preliminary study, tetrapotassium pyrohposphate (TKPP) appeared to be an effective frost preventing chemical for temperatures greater than about 25°F (-4°C) on bridge decks. In addition, if there was no rainfall, it was found to be effective for periods of up to two weeks without reapplication.

In this second study, it was difficult to evaluate the relative effectiveness of the TKPP on the California state highway bridges. This is because, for safety reasons, the chemical had to be applied to the whole surface of the bridge deck. Therefore, even though conditions were such that frost would form on the rails but not on the deck, testing of frost prevention was inconclusive. No "control" area could be provided wherein part of the deck would not receive application of the chemical. However, testing on one-half of a county bridge deck confirmed that TKPP was effective in preventing frost. This does negate the fact that in previous work, an application of the liquid TKPP to a dry pavement would, by itself, melt about one inch (2.5 cm) of ensuing snowfall.

Because of the high cost of TKPP, it is only considered for use on bridge decks to inhibit formation of frost, where temperatures rarely go below 25°F (-4°C). Chloride type salt still remains the most economically feasible method for controlling ice on the many miles of highway pavement in snow areas.

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Field Tests - Skid Testing

Skid tests were performed using solutions of sodium chloride, tetrapotassium pyrophosphate (TKPP) and urea on both concrete and asphalt concrete pavements. Work with the towed skid test trailer, ASTM Test Method E274-65T, showed that this method was not applicable for evaluating the effect of different solutions on pavement friction. (See later discussion.) This was because the test method requires the application of water which overshadows the presence of the chemical. A skidding car method was determined to be the best test method available to Maintenance Superintendents for evaluating TKPP on pavement surfaces[10]. Theoretical analysis and field tests suggest that if a vehicle that is traveling at 10 mph can stop in less than 8 feet of locked wheel braking, the pavement can be considered as not being slippery. Limited test results using the skidding car method indicate that individual applications of up to 0.01 lbs./sq.ft. of 30% TKPP solution will not significantly affect the slipperiness of the roadway. However, much depends upon the surface texture of the pavement because with a smooth pavement, even plain water can be a hazard.

Initially, the field tests of the TKPP solution encompassed the application of sand at the same time. It was found that the sand application itself caused the deck to be "slippery" and this operation was discontinued. Apparently sand is effective for packed snow and ice, but not necessarily satisfactory for wet or frosty conditions except as a "blotter".

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Effect of TKPP on Glass and Asphalt Concrete

Preliminary tests on automobile windshield glass indicate that 30% solution of TKPP (with a corrosion inhibitor of lime) had no effect on the tested glass.

A limited test on asphalt concrete briquets that were cycled between immersion in a 60% TKPP solution and drying in a 140°F (60°C) oven have shown no visually apparent undesirable effects.

Sodium Formate and Asphalt Concrete

Visually, test results indicate that sodium formate has little adverse effect on asphalt concrete.

Concrete Durability

To test concrete durability, length change was measured and physical appearance was noted when samples were alternately oven dried for 7 days in a 140°F (60°C) oven and immersed for 7 days in a solution of the chemical under consideration. The results of this test are as follows:

1. Both 4-1/2-sack and 7-sack air entrained concrete mixes will deteriorate when alternately immersed in a saturated sodium chloride solution.
2. Both 4-1/2-sack and 7-sack air entrained concrete mixes suffer no apparent deterioration when alternately immersed in a solution of plain tap water, saturated urea solution, or a 60% TKPP solution.

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TKPP and the

Corrosion of Steel

Steel immersed in a 5% solution of TKPP, with a corrosion inhibitor consisting of 2% lime, resulted in an insignificant corrosion rate of 0.053 mils per year. A 3% sodium chloride solution resulted in a corrosion rate of approximately 4 miles per year, while in distilled water, steel corroded at a rate of 6.0 mils per year.

It should be pointed out that TKPP is apparently not readily absorbed by concrete. Therefore, the corrosivity of this chemical to steel would probably be limited to bare steel on spray equipment or vehicles.

Field Skid Testing

Towed trailer skid tests were performed on all bridges being used in the field study to determine skid characteristics of the surface prior to applying chemicals. However, the towed skid test trailer (ASTM Method E274-65T) did not show the effect of the different chemicals on the slipperiness of the pavement. The towed trailer places a calibrated stream of water between the skidding tire and the road surface. As most chemicals used are water soluble, the stream of water apparently dilutes and/or removes the chemicals from the wheelpath. Also, no relationship was found between the application of the chemical and the skid number of the road surface.

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Since the commonly used skid testing devices did not show the true effect of the chemical, it was decided to try the skidding car method[10]. This method consists of measuring the length of skid of a standard sedan with locked wheels. The automobile was equipped with a powder actuated marking device connected to the brake pedal. The test speed used was 10 mph. The distance between a chalk mark fired on the pavement occurring at the instant of wheel lock and another one made after stopping, is the measure of skid resistance. The specially mounted speedometer to more easily control the test speed is shown on Figure 1, while Figure 2 shows the special marking devices mounted on the automobile bumper.

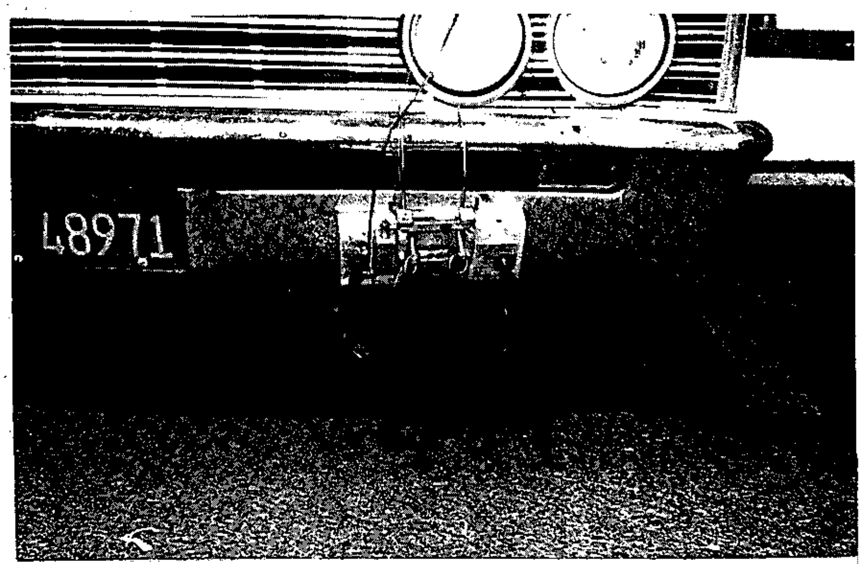

Figure 1. Two-shot marking device mounted on test vehicle.

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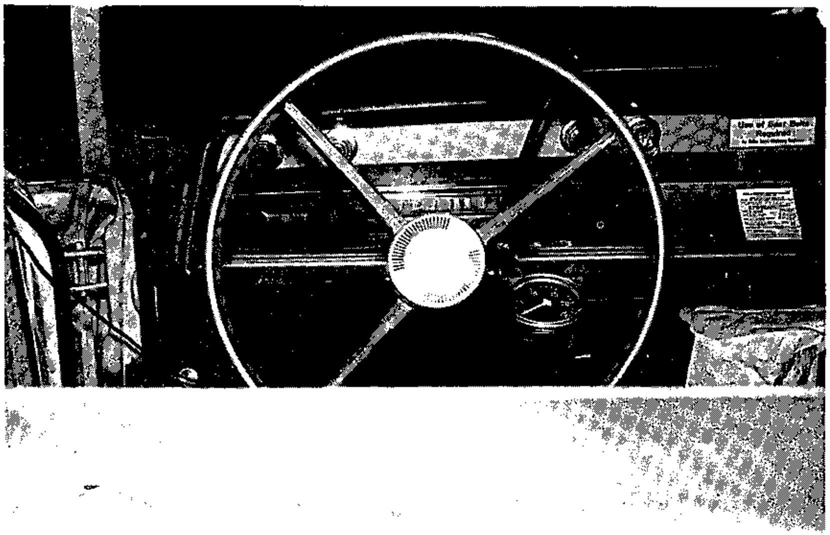

Figure 2. A special 0-30 mph speedometer is mounted adjacent to the steering wheel to better control the 10 mph test speed

After several trials it was decided that a "go - no go" test result for the effect of the deicing chemical on the pavement should be used. The criterion for the test was that the application of the chemical should not cause a serious degradation of the coefficient of friction of the pavement surface and the maximum average stopping distance should not exceed 8 feet. In this regard the following equation was used

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to calculate the maximum allowable stopping distance from a vehicle velocity of 10 mph:

$$f = \frac{V^2}{30S} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Wherein: V = miles per hour (10)

S = distance travelled before stopping, feet

f = coefficient of friction

(A value of 0.40 for this coefficient was selected as being reasonably good.)

Using a speed of 10 mph and an "f" of 0.40, calculation indicates that the pavement would have a sufficiently great skid resistance if the vehicle does not skid more than about 8 feet when braking from a velocity of 10 mph.

As indicated by Table 1, the greatest influence on the skid distance on a portland cement concrete deck was whether or not it was wet or dry. However, in all cases, the average skid distance was less than 8 feet, therefore the deck surface of these bridges was considered to be of adequate roughness for safe application of water or the deicing chemical used (TKPP).

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When TKPP was applied with a hand sprayer on a relatively smooth AC covered bridge deck, one skid out of five was greater than 8 feet. A series of four tests where the bridge deck surface was wet (due to high humidity), resulted in one test out of four being over 8 feet. In this case, the very old irregular surface of the bridge combined with the hand application of the chemical produced puddles of chemical and water on the surface, and resulted in some of the tests exceeding a distance of 8 feet. In some cases where skid resistance of the deck surface is already borderline, the application of the deicing solution (or water) can lower skid resistance below the desired level.

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Table 1

Skid Tests

	SURFACE CONDITION				
Condition	Dry	Wet[2] (Water)	Wet[3] (Chemical)	Wet[4] (Chemical-Humidity)
PCC Bridge Deck[1]				
Avg. Skid Distance, Feet[1]	4.7	6.3	6.3	6.6
No. Tests	13	8	20	2
AC Overlaid Bridge Deck				
Avg. Skid Distance, Feet[1]	5.4	5.7	6.8	7.1

Note: [1]Skid tests are braking distance when vehicle velocity is 10 mph.

[2]Sprayed to have continuous film of water.

[3]Immediately after applying 0.01 lb./sq.ft. of TKPP

[4]Deliquescent effect of chemical in producing a wet deck during high humidity

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LABORATORY TEST DETAILS

Sodium Formate and Asphalt Concrete

In this test, asphalt concrete briquets were cycled between 7 days of immersion in a saturated sodium formate solution and 7 days of drying in a 140°F oven. Also, one sample which was made up of approximately a 1-1/4" thick layer of asphalt concrete on top of a 1-foot square concrete block, was also cycled. After five alternate wet and dry cycles, no serious deterioration occurred in the AC surfacing or briquets. There did not appear to be any loss of bond between the AC and the concrete. There was, however, severe deterioration of the exposed concrete surface of the 1-foot square block.

PCC Concrete Durability

In order to determine to what degree the various deicing chemicals could adversely affect concrete, 84 cylinders (4-1/2 x 9 inches) with imbedded gage plugs at each end were subjected to alternate immersion tests. Changes in length

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and observations of physical distress were noted. The cylinders were made from two mix designs; one having 4-1/2 sacks of cement per cubic yard at 2-3/4-inch slump and 5.8% entrained air, and the other having 7 sacks of cement per cubic yard at 4-inch slump with 4.5% entrained air. All cylinders were cured for a minimum of 28 days by complete immersion in tap water at room temperature, then oven dried at 140°F (60°C) for 28 days in a forced draft oven. In one series the specimens were alternately completely immersed in the solutions for 7 days followed by oven drying 7 days at 140°F (60°C). Changes in length and weight were measured and visual distress noted after each cycle. In a second series, other specimens were continually partially immersed (2 inches) in the solutions with no oven drying. Figure 3 shows the results of alternate immersion-oven drying on length change for each of the solutions used. A summary of these tests is as follows:

A. Both 4-1/2 and 7-sack concrete cylinders were not significantly affected after 41 cycles of wet-dry tests when alternately submerged in tap water.

B. Concrete cylinders cycled and fully submerged in a saturated sodium chloride soltuion were first observed to have scaling of the surfaces of all cylinders after

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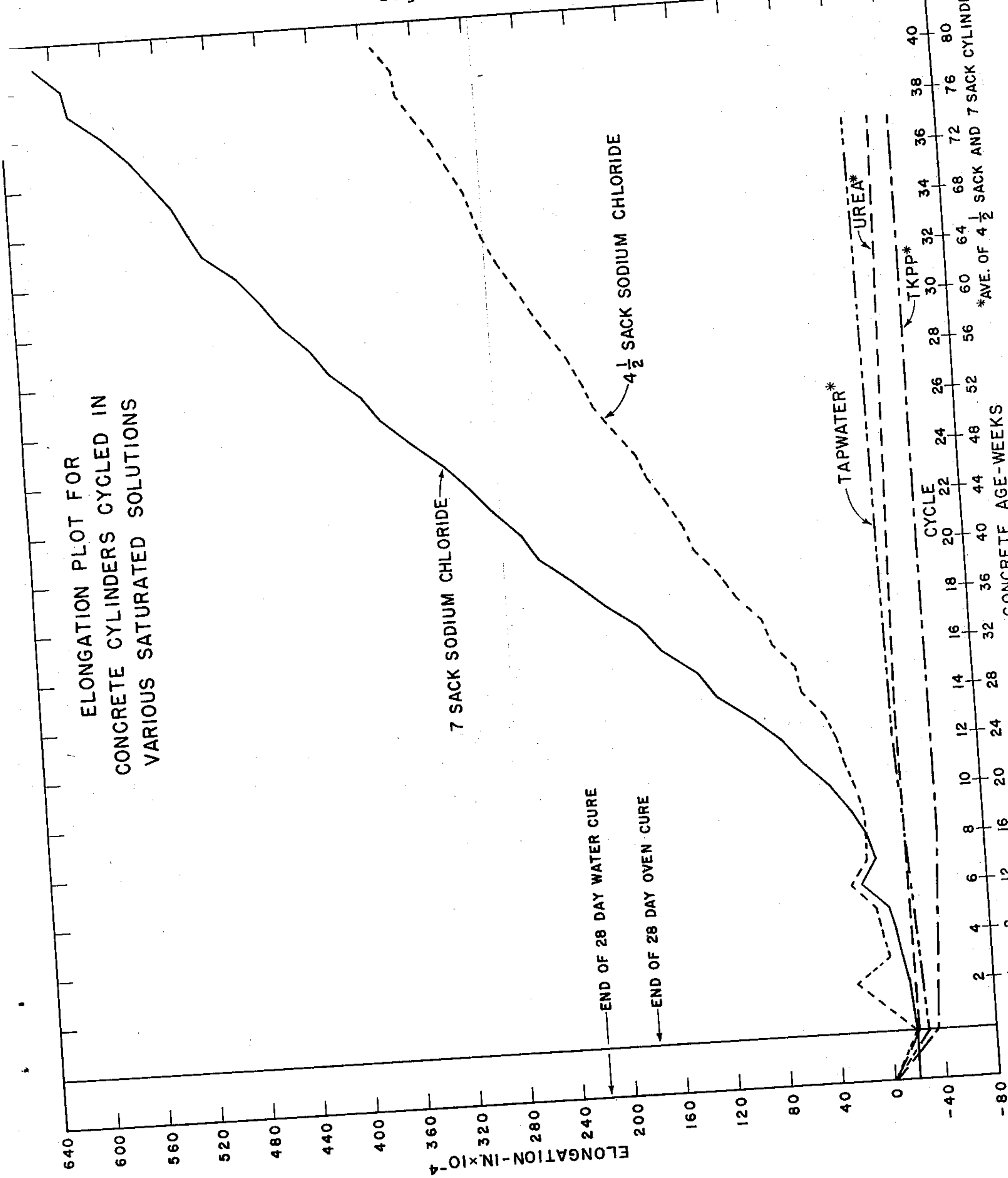
Figure 3



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the third cycle. A progressive deterioration of the surface continued for approximately 80 cycles. After 80 cycles, the deterioration was so severe that the test was discontinued. The typical deterioration of the 7-sack concrete that was alternately immersed in the sodium chloride solution is shown on Figure 4.

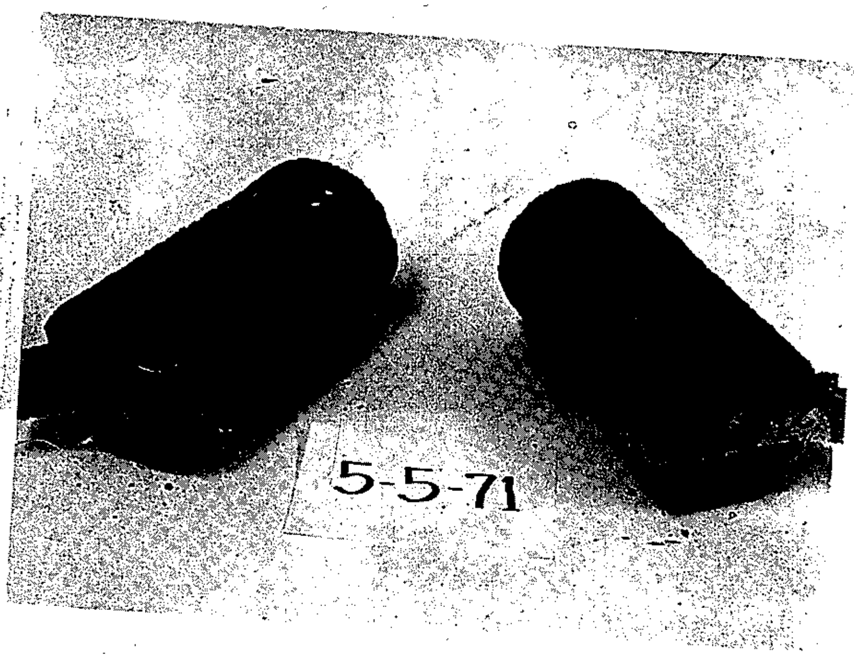

Figure 4. A-1 and A-2 - 7-sack concrete cylinders after 40 cycles in a sodium chloride solution

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C. No adverse effect was noted on the cylinders which were partially immersed in tapwater, saturated sodium formate, or saturated sodium chloride.

D. After 3 cycles of complete immersion and oven drying in the sodium formate solution, the 7-sack concrete exhibited severe distress. (See Figure 5.)

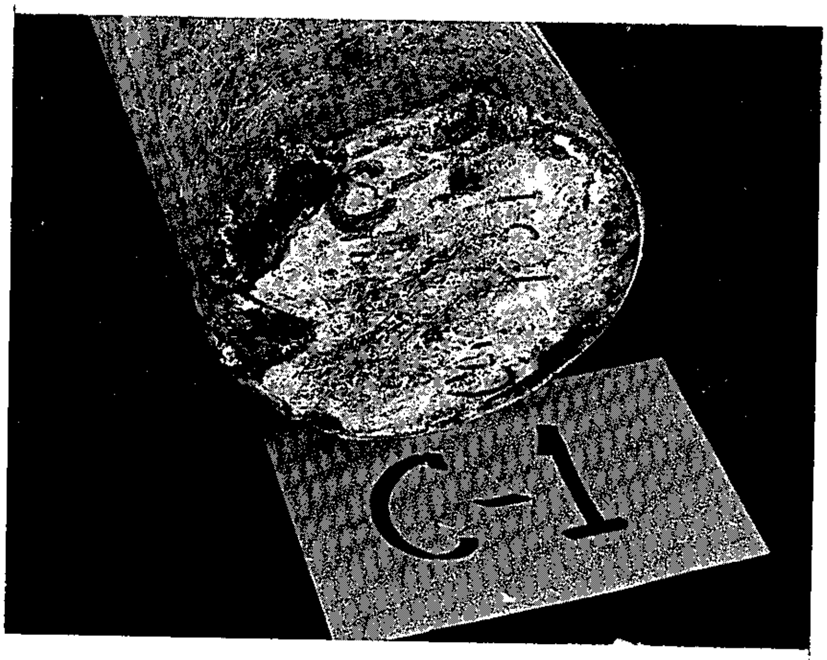

Figure 5. Appearance of concrete after three cycles of exposure to sodium formate

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E. After 25 cycles in a 60% solution of TKPP, no deterioration was evident on either the 4-1/2 or 7-sack concrete cylinders.

F. After 25 cycles in a saturated urea solution, only negligible surface scaling was observed on the 4-1/2 and 7-sack concrete cylinders.

Field Trial of TKPP

The chemical TKPP underwent field trials during the winters of 1971 and 1972 in seven geographic areas of California. The test areas included locations where only the bridge decks would become frosty, and there was no snowfall, and in other areas where heavy snow and icing occurred. In these latter locations, TKPP was not effective in this test series because of the low temperatures encountered (less than 25°F (-4°C)).

The following is a summary of the observations concerning the effectiveness of TKPP in the various locations:

Location 1
Russian River Bridge No. 10-182
Elevation - 710 feet

TKPP was applied at a rate of 0.01 lb./sq.ft. of deck and remained in place for 15 days. No frost occurred after

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application at this location. The chemical appeared to be "available" because there was evidence of formation of TKPP crystals upon evaporation of the water, and the pavement appeared wet in the early morning due to the deliquescent effect of the chemical. No evidence of pavement slipperiness was noted. A "wet" appearance of the deck has been evidence that TKPP has prevented or controlled frosting.

Location 2

Grass Valley Creek

Bridge No. 5-10 - PCC deck, Elevation 2200 feet

Bridge No. 5-13 - AC overlay, Elevation 2110 feet

A spray solution of 30% TKPP was applied at a rate of 0.01 lb./sq.ft. Two days after the application, frost conditions were present as the temperature was 27°F (-3°C) and the relative humidity reached about 100%. The decks did not frost over; however, they were wet due to the deliquescent effect of the chemical. On both of these structures, at a later date, the TKPP powder was applied in conjunction with 1-1/2 cu.yd. of sand. The wet sand froze to the bridge decks.

For these same decks, the normal application of chemical solution was applied and was reported to be effective for a period of 7 days because of the early morning wet appearing decks.

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A second application of the chemical was made and three days later the temperature was 22°F (-6°C) and frost was observed on the ground adjacent to the bridges. The bridges at this time were frost-free but "wet" appearing. No pavement slipperiness was observed.

On Bridge 5-10, the average skid distance on dry pavement was 4.5 feet, while on wet pavement containing TKPP, the average distance was 4.8 feet.

On Bridge 5-13, the average skid distance was 3.5 feet on dry pavement and 4.5 feet on wet pavement containing TKPP.

Location 3
Sacramento Weir,
Bridge 22-32 With Overlay

A 30% solution of TKPP was applied at a rate of 0.01 lb./sq.ft. of deck surface. Immediately after applying the chemical, it was found that a pickup truck could quickly stop on the bridge. However, within 10 minutes after applying the chemical, a light application of sand was placed on the bridge deck. The sand caused the pickup truck to slide on the bridge deck when the brakes were applied. As soon as traffic whipped the sand from the travelled way, the deck was no longer slippery. Sand was not reapplied with the deicing chemical at this location.

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Two days after the application of the chemical, the bridge was under frost conditions as the temperature was 29°F (-2°C) and frost was observed on the guardrails. The bridge deck had a wet appearance. It was necessary to salt and sand nearby bridges. On this bridge, at one time one day after the application of the chemical, the maintenance foreman reported that the pavement was slippery when the pavement appeared wet. The early morning temperature was about 27°F (-3°C). It is possible that the chemical was too heavily applied when considering the residual chemical that was still in place on the deck. It was effective in preventing frost during frost conditions on this deck for a maximum period of 12 days when there was no rainfall.

Location No. 4
Wheatland Bear River Bridge
PCC Deck; Elevation - 108 feet

One standard application of chemical was observed to be effective on this bridge for an estimated period of 19 days. Even though this bridge showed evidence of frost on the rails but not on the deck during this time period, another bridge about 7 miles distant received 20 applications of salt and

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sand. This bridge had an average skid number of Sn_{40} of 46, while the skid distance on the dry deck was 4.8 feet. When wet with plain water, the average distance was 6.4 feet, and wet with a TKPP solution, the average distance was 6.3 feet.

Location 5

Bridge 56-184, Hemet Valley Creek

Elevation 4360 feet, AC Overlay

One standard application of chemical was placed on this bridge deck at time intervals of 6, 9, and 7 days. During this period, the deck had a wet appearance in the early morning with no frost present on the deck. The minimum morning temperature was about 24°F (-4°C) for an estimated 4 days. Adjacent bridges required salt and sand for frost prevention. No slipperiness of the deck was observed by the maintenance personnel.

Location No. 6

Bridge 39-44, Bradley Overhead

Dist. 10, Elevation 170 feet,

AC Overlay

TKPP was applied and thought to cause slipperiness. Use of chemical was discontinued.

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Location No. 7

G. S. Housely Bridge, Sutter County

Corrugated Steel Plank Deck with AC

Riding Surface

The bridge is a county-owned bridge that does not normally receive deicing chemicals. Therefore, TKPP was applied only to the northbound lane, and the southbound lane was left untreated as a control. The typical means for applying the chemical is shown in Figure 6.

Two days after TKPP solution was applied, the southbound lane was frosty (no chemical), while the treated northbound lane was frost-free but wet. The air temperature was 29°F (-2°C), while the relative humidity was 90%. The typical appearance of this bridge during the test is shown on Figure 7.

The structure was maintained in a frost-free condition during the entire test period. The early morning temperatures did not fall below about 24°F (-4°C).

The results of using the chemical on the skid resistance of this deck surface is shown on Table 1, AC Overlaid Bridge Deck.

A few trial skid tests using the "skidding car test" were made on the frosty side of this bridge. It was found

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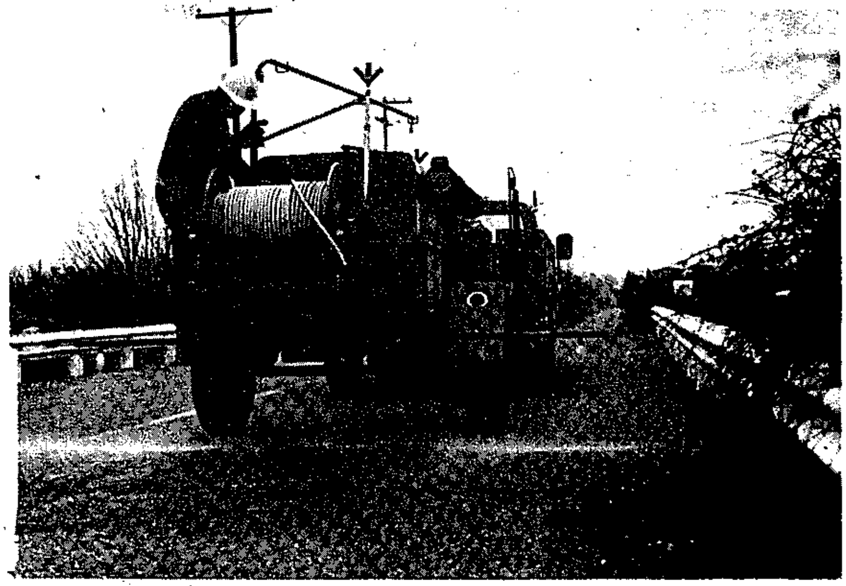

Figure 6. Application of 30% solution of TKPP

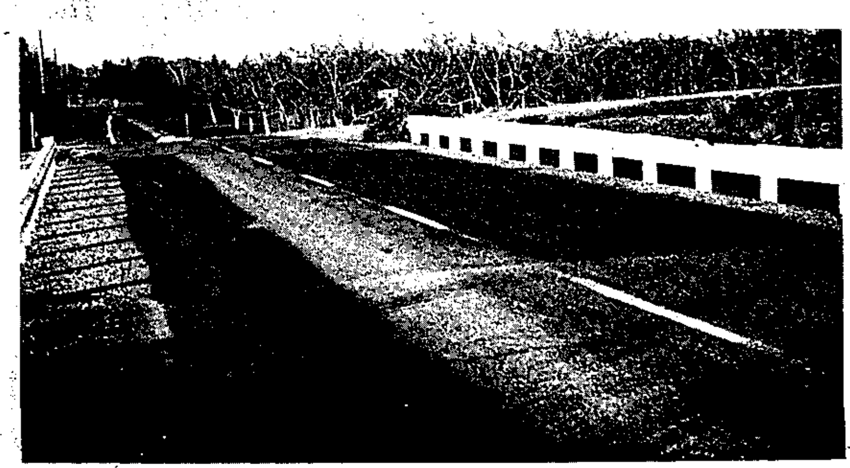

Figure 7. Sutter County Test Bridges, looking north.

30% TKPP has been applied to the right side of the bridge. Note frost on left side.

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that there was no significant difference in the skid distance between the frosty or wet bridge deck. However, this would not be true if the deck were icy or had a layer of snow. In this case, the frost apparently caused little danger to traffic as far as skidding was concerned.

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DISCUSSION

The tests show that a 30% solution of TKPP applied at a rate of 0.01 lb./sq.ft. of bridge deck surface is an effective frost preventative in mild climates. However, whether or not the chemical affects the slipperiness of the pavement more than water does depends upon the smoothness of the pavement and perhaps the thickness and hardness of the frost layer, if present.

If the skid test shows that a wet or dry deck can result in a skid distance exceeding 8 feet, then the application of any liquid, including plain water, can create a hazard. For example, on the Bear Creek Bridge in District 10, the average skid distance on the dry deck was 11 feet while wet with a TKPP solution, the average distance was 22 feet.

The skidding car test can be used in other ways. For example, in one isolated test, the effectiveness of multiple applications of sand on the skid resistance on compacted snow was investigated. It was found that there was no significant improvement on skid distance when sanding was done three times instead of once.

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It is probable that the skidding car test may be useful in determining when to request the skid trailer so as to determine the skid number of the pavement, or as a means to set up a priority for the chip sealing of a pavement to increase the skid number.

Based upon this study, it appears that in some cases, salting and sanding of bridge decks may be done as matter of "insurance" rather than as a result of actual need. For example, in one maintenance area it was found that the actual application rate of salt was an average of 0.001 lb./sq.ft. of deck area. This amount of salt is ineffective for the prevention of hazardous frost conditions. However, the multiple applications of the salt is the cause of much bridge deck deterioration.

Presently, it is not appropriate to make a cost comparison between the use of salt and TKPP to control frosting of decks. In one maintenance area, it is estimated that because of the lasting effect of TKPP, a maintenance crew could reduce the number of "salting" patrols by more than 50% by using the TKPP solution. Also, the patrols could be made during normal working hours instead of beginning them at 4:00 AM.

It should be emphasized that TKPP is only being considered for those locations which are free of ice and snow. Such areas are normally the valley locations in California

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where only the bridge deck frosts over and requires the use of a chemical to control frosting.

In the previous work, it was observed that the most effective use of any tested deicing chemical was to apply it in liquid form prior to the conditions of frost and snow. However, once the snow was packed, crystals of a deicer were needed to penetrate and break up the physical structure of the ice or snow.

It has been related to the authors that sodium formate may be a lesser source of physical discomfort than calcium chloride when skin or eye contact occurs. Therefore, for ice melting conditions when the temperature is less than about 15°F to 20°F (-9°C to -7°C) where calcium chloride is usually used, sodium formate may prove to be a satisfactory alternative where the quantities needed are not too great. Because of the potential damage that might occur to the concrete by the use of sodium formate, its use is not recommended.

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